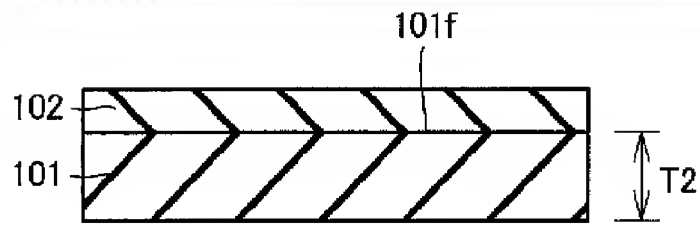
JAPANESE [JP,2003-277183,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

Drawing selection Drawing 2



[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]Especially this invention relates to a quality diamond single crystal object and a manufacturing method for the same with the large area used for a semiconductor material, electronic parts, an optic, etc. about a manufacturing method of a diamond single crystal, a diamond single crystal board, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]The diamond is provided with many outstanding characteristics which otherwise do not look at a class as a semiconductor material, such as high heat conductivity, a high electron and hole mobility, high dielectric breakdown pressure-proofing, low dielectric loss, and a large band gap. In particular, in recent years, the ultraviolet light emitting device which harnessed the large band gap, a field effect transistor with the outstanding high frequency characteristic, etc. are being developed. In order to apply a diamond as a semiconductor, a diamond single crystal board is fundamentally needed. As for this diamond single crystal for semiconductor investigation, all have been mostly manufactured with the high-temperature-high-pressure synthetic method till the present. Even if it compares with a natural single crystal the diamond single crystal obtained by a high-temperature-high-pressure method, it has the feature

from which a good crystalline single crystal is obtained. However, since the ultra-high pressure synthesizer unit used by a high-temperature-high-pressure method is large and its device size is expensive, there is a limit in reduction of the manufacturing cost of a diamond single crystal. Since the single crystal size obtained is proportional to device size, 1-cm class of the size of a parenchyma top is a limit.

[0003]In order to solve fundamentally above-mentioned single crystal size and the problem of a manufacturing cost, the single crystal manufacturing method using epitaxial growth by a chemical-vapor-deposition (CVD) method is being developed. Generally epitaxial growth is divided into the substance which grows, the homoepitaxial growth whose single crystal is grown up on a monocrystal substrate of the same kind, and the heteroepitaxial growth which grows up a single crystal on the monocrystal substrate of a different kind.

[0004]In homoepitaxial growth, epitaxial growth is performed from the gaseous phase to the tabular diamond single crystal which is called Ib type obtained by the high-temperature-high-pressure method and which contains nitrogen as an impurity in many cases. The single crystal of the high grade which is larger size than the IIa type single crystal which does not contain the nitrogen impurity obtained by a high-temperature-high-pressure method by this method, and does not contain nitrogen in a film is obtained.

[0005]On the other hand, the example which began Si and SiC and grew epitaxially on single crystals, such as Pt and nickel, is reported, for example to JP,63-224225,A, JP,2-233591,A, and JP,4-132687,A by heteroepitaxial growth. By using as a substrate an above-mentioned material which is easy to obtain the monocrystal substrate of a large area as compared with a diamond, large area-ization of a diamond single crystal is expectable.

[0006]

[Problem(s) to be Solved by the Invention]There is a point which poses a problem by above-mentioned epitaxial growth when obtaining a quality diamond single crystal with a large area. The remaining stress resulting from the difference of a coefficient of thermal expansion with a substrate or the mismatching of a lattice is accumulated, and there are modification of a film or exfoliation, and a phenomenon in which a film and a substrate break further as the thickness of an epitaxial film becomes thick. In heteroepitaxial growth, essential solution is difficult for these from the difference of the basic physical properties of an epitaxial film and a monocrystal substrate. If a substrate becomes a large area, the deformation will become large in proportion to area, and the probability of being divided also increases.

[0007]On the other hand, these days also in homoepitaxial growth, the phenomenon in which remaining stress is accumulated into an epitaxial film is reported by the collection [of 12th time of new diamond forum sponsorship diamond symposium lecture gists] p74 lecture number P17, for example.

Even if this phenomenon grows homoepitaxially on Ib type diamond substrate, it has suggested having hetero epitaxial growth actually. Under the present circumstances, although it is a several millimeter square film formation surface product, when homoepitaxial growth of a future more big area is realized, it is expected that the same problem as heteroepitaxial growth which was already described arises.

[0008]Then, this invention is made in order to apply a vapor-phase-synthesis diamond to the electronic industry material etc. which are represented by the semiconductor. The purpose of this invention is to solve an above-mentioned problem and to provide a manufacturing method of a diamond single crystal with it, a diamond single crystal board, and a manufacturing method for the same. [a large and area and] [quality]

[0009]

[Means for Solving the Problem]After growth of a single crystal of a diamond had little influence of a substrate relatively, and this invention person found out that phenomena, such as modification of a diamond single crystal, exfoliation, or a crack, could be controlled to minimum, when thickness used a tabular seed crystal of 100 micrometers or less. This tabular single crystal may be various single crystal materials including a diamond. A single crystal in which heteroepitaxial growth of a diamond is possible may be formed on a single crystal of arbitrary material, or polycrystal. For example, what formed Pt single crystal on Si polycrystal may be used. Or a diamond single crystal may be directly grown up on polycrystal of arbitrary material. As there is thickness of a seed crystal at 100 micrometers or less, it is more desirable, but a mechanical strength becomes weaker, so that it becomes thin, and there is a possibility that it may be changed or damaged at the time of handling. That is, suitable thickness changes in 100 micrometers or less with construction material of a seed crystal. If a diamond single crystal is grown up by an above-mentioned method, even if area of an epitaxial film becomes greatly and thick, neither a crack nor modification can arise, but an epitaxial film can be grown up with high quality.

[0010]A tabular seed crystal is good to use a diamond single crystal board and a diamond single crystal board desirably manufactured with a vapor phase synthetic method. If a diamond single crystal is used for a substrate for single crystal growth, modification and damage which are growing homoepitaxially and originate in a difference of a physical property of a substrate and a film can be controlled. An I-beam by high-temperature-high-pressure composition even if this diamond single crystal board is a natural single crystal, Although it may be II type single crystal, if it is the diamond single crystal board manufactured especially with a vapor phase synthetic method, it will be growing homoepitaxially "thoroughly", and since a difference of the physical properties of a substrate and a film becomes very small, it is preferred. As a vapor phase synthetic method to apply, they may be one or those combination in a hot filament CVD method, a microwave plasma CVD method, a direct-current-plasma CVD

method, or a burning flame method. Vapor phase synthetic methods other than this are also realizable.
[0011]Although the thickness of a substrate should just be 100 micrometers or less, since the mechanical strength of a diamond is strong, it is maintainable as an independent substrate at least 50 micrometers or less. If thickness grows up a diamond single crystal from a not less than 10-micrometer diamond single crystal board of 50 micrometers or less, it can suppress to the minimum that an epitaxial film is influenced by a substrate, and also when thickness is increased, it will become small to such an extent that modification of a substrate and a film can disregard almost.
[0012]It is preferred that not less than 10 ppm 500 ppm or less of hydrogen atoms are contained in a diamond single crystal board by an atomic ratio to a carbon atom. When a diamond is grown up with a vapor phase synthetic method in a hydrogen atmosphere, hydrogen will usually be incorporated during a crystal. this invention person performed a fixed quantity of quantity of hydrogen incorporated into a crystal at the time of epitaxial growth, and it found out that the value was settled in the range of 500 ppm or less more than 10 ppm (parts per million) in an atomic ratio to a carbon atom. That is, if a diamond single crystal board of this impurity concentration is prepared, property values of a [an epitaxial film and a diamond single crystal board] which grow from here including a grating constant correspond, and they can control modification of a substrate and a film.
[0013]It is preferred that a plane direction of a grown surface of a diamond single crystal board grows to {100} sides. While {100} sides had maintained crystallinity also on conditions that a growth rate is quick, as compared with other fields, since it is an elastic field relatively, a monocrystal substrate of the good surface tends to be obtained by polish etc. so that single crystal growth is possible. Since it is a field which cannot incorporate impurity elements including nitrogen easily out of the gaseous phase, it is also expectable to control modification after growth of a single crystal.
[0014]It is preferred that the diamond full width at half maximum by an X-ray diffraction method of a diamond single crystal board used for epitaxial growth in a manufacturing method of a diamond single crystal of this invention is 400 or less seconds 5 seconds or more. The crystallinity of a diamond single crystal board used for epitaxial growth is so preferred to good epitaxial growth that it is better.
[0015]A result of having investigated correlation of the crystallinity of a diamond single crystal board, and the crystallinity of an epitaxial film grown-up on it with an X-ray diffraction method which is one of the ways this invention person evaluates crystallinity quantitatively, When half breadth of a diamond peculiar peak (what is called a rocking curve) of a crystal was in a mentioned range, it was shown clearly that good epitaxial growth is possible. A hydrogen atom and a carbon atom are included, not less than 10 ppm 500 ppm or less of hydrogen atoms are contained by an atomic ratio to a carbon atom, and, as

for a diamond single crystal board of this invention, it is preferred that thickness is 100 micrometers or less. As already stated, a diamond single crystal contained as an impurity has a fixed quantity of useful hydrogen atoms as a substrate of homoepitaxial growth by a vapor phase synthetic method. If that thickness is 100 micrometers or less, even if it grows epitaxially using this substrate, a diamond single crystal will not change and it will not break. If it is the hydrogen quantity within the limits of this, it is applicable to various diamond semiconductors as it is. As for size of a diamond single crystal board, it is preferred that a plane direction of a main table side which is a field in a field which is not less than 10 mm and constitutes a substrate where a length of at least one side is the largest is {100}. If there is a monocrystal substrate of a large area, homoepitaxial growth can aim at enlargement more. It becomes easy to perform a semiconductor-oriented micro-processing process etc. If a plane direction of a main table side of a substrate is {100}, next epitaxial growth and surface mechanical processing will become easy.

[0016]As for a diamond single crystal board of this invention, it is preferred that the diamond full width at half maximum by an X-ray diffraction method is 400 or less seconds 5 seconds or more. If a diamond peak of an X diffraction which is a crystalline index is within the limits of the above as already stated, even when quality epitaxial growth will be attained after that and it will apply this substrate to a single crystal, there is little fault resulting from crystallinity.

[0017]In a manufacturing method of a diamond single crystal board of this invention, preferably, thickness shall carry out etching removal of the not less than 100-micrometer diamond single crystal board by reactive ion etching, and shall be 100 micrometers or less in thickness.

[0018]When obtaining the above-mentioned diamond single crystal board, a process of making thin a diamond single crystal board with a large area to 100 micrometers or less in thickness poses a problem. That is, in mechanical polish, for a crack by polishing load, etc., it is difficult for thickness to be 100 micrometers or less, and if area of a single crystal becomes large, it will become more difficult. A possibility that cutting by high output laser will also be accompanied by damage to a substrate by this board thickness is high, and cutting of area more than 1 cm^2 is very difficult primarily.

[0019]this invention person showed clearly that the thickness can be made thin to 100 micrometers or less also with a diamond single crystal board of a large area using reactive ion etching (RIE) which is an un-mechanical processing process. Local processing is possible for a RIE process by using a mask, and when a substrate is an un-parallel crystal, it can be used as a substrate of a parallel thin film after processing. Even if it is except RIE, a diamond single crystal board can be etched by using laser ablation, ion beam etching, etc.

[0020]Thickness carries out vapor phase epitaxy of the diamond single crystal of 100 micrometers or less to a diamond single

crystal object, and a manufacturing method of a diamond single crystal board of this invention carries out etching removal of the diamond single crystal object to it by reactive ion etching after that. Even if it is a case where began a diamond single crystal object manufactured by a high-temperature-high-pressure method, and a diamond single crystal is grown epitaxially on a diamond single crystal object manufactured except a vapor phase synthetic method, such as a natural single crystal, Remaining stress is accumulated as are already stated and an epitaxial film becomes thick, and it may be accompanied by modification and damage to a substrate or a film. If area grows up a diamond single crystal from a large area monocrystal substrate of the 1-cm^2 class especially, the possibility of modification or damage will increase. Remaining stress accumulated even if it is a large area single crystal, if this invention person is [thickness of an epitaxial film which carries out vapor phase epitaxy on a monocrystal substrate] 100 micrometers or less as a result of research was small, and it was shown clearly that it is accompanied by neither modification nor damage. It was very difficult to grind a monocrystal substrate which has remaining stress using [limitation] the usual mechanical polishing work in art by the present, and to obtain self-supported film which consists only of epitaxial films.

[0021]In order for this invention person to use this epitaxial film as an independence board, when removing a monocrystal substrate by an above-mentioned method, thickness discovered that a vapor-phase-synthesis diamond single crystal board of 100 micrometers or less was obtained. This monocrystal substrate can be used for an already described manufacturing method of a diamond single crystal. It is applicable also as a substrate for diamond semiconductors then. Even if it is except RIE, a diamond single crystal board can be etched by using laser ablation, ion beam etching, etc.

[0022]As for a diamond single crystal grown up on a diamond single crystal object, it is preferred that a rate of a hydrogen atom is not less than 10 ppm 500 ppm or less in an atomic ratio to a carbon atom including a hydrogen atom and a carbon atom. By storing hydrogen impurity quantity in a mentioned range, a good crystalline monocrystal substrate can be obtained comparatively. This substrate can be used for epitaxial thick film growth or semiconductor application.

[0023]In a manufacturing method of a diamond single crystal board of this invention, plane directions of an etching surface of a diamond single crystal board are {100} sides preferably. If plane directions of an etching surface are {100} sides, a diamond single crystal object can be beforehand processed mechanically preparatorily before etching, and accuracy of a processed surface seen at the whole process can be raised. After etching can provide good epitaxial growth with this substrate as it is.

[0024]In a manufacturing method of a diamond single crystal board of this invention, etching gas used for reactive ion etching consists of mixed gas with oxygen, carbon fluoride, or argon

preferably. The mixture ratio of oxygen is below the whole 50 volume %. As for a pressure of the mixed gas, it is preferred that it is 6.7 Pa or less.
[0025]High frequency voltage is impressed to inter-electrode [which has been arranged in a vacuum housing], plasma is generated, and roughness of a substrate face after etching poses a problem in a general reactive-ion-etching process of etching a diamond substrate, with produced ion. It is clear that roughness on the surface of etching is dependent on an etching gas kind, and percentage and also a pressure until now. As a result of advancing research in detail, this invention person became final and conclusive an etching condition settled in surface roughness which does not pose a problem, when growing epitaxially after etching. The diamond single crystal board etched by above-mentioned composition gas and a pressure can grow homoepitaxially to an etching surface as it is after that.
[0026]A manufacturing method of a diamond single crystal of this invention made by the above knowledge is provided with the following.
A process which thickness prepares a tabular seed crystal of 100 micrometers or less.
A process of forming a diamond single crystal with a vapor phase synthetic method on a tabular seed crystal.

[0027]Since thickness grows up a diamond single crystal with a vapor phase synthetic method on a tabular seed crystal of 100 micrometers or less, the manufacturing method of a diamond single crystal according to this invention provided with such a process can provide a diamond single crystal which neither modification nor a crack produces.
[0028]A process for which a tabular seed crystal is prepared includes preferably a process for which a diamond single crystal board is prepared.
[0029]A process for which a diamond single crystal board is prepared is preferably provided with a process for which a diamond single crystal board with greater than 100 micrometers in thickness is prepared, and a process that some diamond single crystal boards shall be removed and thickness shall be 100 micrometers or less.
[0030]A process of removing some diamond single crystal boards includes preferably a process of removing some diamond single crystal boards by reactive ion etching.
[0031]A process for which a diamond single crystal board is prepared includes preferably a process at which thickness forms a diamond single crystal board of 100 micrometers or less with a vapor phase synthetic method on a diamond single crystal object, and a process of removing a diamond single crystal object.
[0032]A process of removing a diamond single crystal object includes preferably a process of removing a diamond single crystal object by reactive ion etching.
[0033]A process for which a diamond single crystal board is prepared includes preferably a process which a rate over a carbon atom and a carbon atom prepares a diamond single crystal board

which contains not less than 10 ppm the hydrogen atom it is [hydrogen atom] 500 ppm or less by an atomic ratio.
[0034]Preferably, main table sides of a diamond single crystal board are {100} sides, and a diamond single crystal is formed on the main table side.
[0035]The diamond full width at half maximum by an X-ray diffraction method of a diamond single crystal board is 400 or less seconds 5 seconds or more preferably.
[0036]Thickness is 100 micrometers or less including a hydrogen atom whose rate of as opposed to a carbon atom and a carbon atom in a diamond single crystal board according to this invention is not less than 10 ppm 500 ppm or less in an atomic ratio.
[0037]Even when growing up a diamond single crystal with a vapor phase synthetic method on it, modification and a crack stop arising in the diamond single crystal in such a diamond single crystal board. This diamond single crystal board is also applicable to a semiconductor device.
[0038]The length of at least one neighborhood is not less than 10 mm preferably. Main table sides which have the greatest area are {100} sides preferably.
[0039]The diamond full width at half maximum by an X-ray diffraction method of a diamond single crystal board is 400 or less seconds 5 seconds or more preferably.
[0040]According to one aspect of affairs of this invention, a manufacturing method of a diamond single crystal board is provided with the following.
A process for which a diamond single crystal board with greater than 100 micrometers in thickness is prepared.
A process that some diamond single crystal boards shall be removed and thickness shall be 100 micrometers or less.

[0041]In a manufacturing method of a diamond single crystal board provided with such a process, thickness can manufacture a diamond single crystal board of 100 micrometers or less from a diamond single crystal board with greater than 100 micrometers in thickness. Therefore, a diamond single crystal object which there is no modification and a crack does not produce can be acquired by manufacturing a diamond single crystal object on this diamond single crystal board.
[0042]Preferably, a process of removing some diamond single crystal boards includes a process of removing a part of monocrystal substrate by reactive ion etching.
[0043]Fields where reactive ion etching of the diamond single crystal board was carried out are {100} sides preferably.
[0044]Gas used for reactive ion etching is mixed gas containing either [at least] carbon fluoride (CF_n) or argon (Ar) and oxygen (O_2) preferably, and the percentage of oxygen in mixed gas is 50% or less in a volume ratio.
[0045]As for reactive ion etching, internal pressure is preferably performed within a container of 6.7 Pa or less.
[0046]A process for which a diamond single crystal board is prepared includes preferably a process which a rate over a carbon

atom and a carbon atom prepares a diamond single crystal board whose thickness is 100 micrometers or less including not less than 10 ppm the hydrogen atom it is [hydrogen atom] 500 ppm or less by an atomic ratio.

[0047]A manufacturing method of a diamond single crystal board according to another aspect of affairs of this invention is provided with the following.

A process at which thickness forms a diamond single crystal board of 100 micrometers or less with a vapor phase synthetic method on a diamond single crystal object.

A process of removing a diamond single crystal object.

In a manufacturing method of a diamond single crystal board according to this invention provided with such a process, thickness can manufacture certainly a diamond single crystal board of 100 micrometers or less by removing a diamond single crystal object. Therefore, modification can obtain a diamond single crystal which a crack does not produce few by growing up a diamond single crystal with a vapor phase synthetic method on this diamond single crystal board.

[0048]A process of removing a diamond single crystal object includes preferably a process of removing a diamond single crystal object by reactive ion etching.

[0049]Fields where reactive ion etching of the diamond single crystal object was carried out are {100} sides preferably.

[0050]Gas used for reactive ion etching is mixed gas containing either [at least] carbon fluoride or argon and oxygen preferably, and the percentage of oxygen in mixed gas is 50% or less in a volume ratio.

[0051]As for reactive ion etching, internal pressure is preferably performed within a container of 6.7 Pa or less.

[0052]A process of forming a diamond single crystal board with a vapor phase synthetic method preferably, A rate over a carbon atom and a carbon atom includes a process of forming a diamond single crystal board whose thickness is 100 micrometers or less with a vapor phase synthetic method, including not less than 10 ppm the hydrogen atom it is [hydrogen atom] 500 ppm or less by an atomic ratio.

[0053]

[Embodiment of the Invention]Hereafter, this embodiment of the invention is described with reference to drawings.

[0054](Embodiment 1) Drawing 1 - drawing 3 are the sectional views for explaining the manufacturing method of the diamond single crystal according to this embodiment of the invention 1. With reference to drawing 1, the diamond single crystal board 101 is prepared first. The diamond single crystal board 101 is provided with the following.

Carbon atom.

The hydrogen atom whose rate over a carbon atom is not less than 10 ppm 500 ppm or less in an atomic ratio.

The length of at least one neighborhood of the diamond single crystal board 101 is not less than 10 mm. 101 f of main table sides which have the greatest area are {100} sides. The diamond full

width at half maximum by the X-ray diffraction method of the diamond single crystal board 101 is 400 or less seconds 5 seconds or more. The thickness T1 of the diamond single crystal board 101 exceeds 100 micrometers.
[0055]With reference to drawing 2, some diamond single crystal boards 101 are removed. That is, 101 f of main table sides are etched. Thereby, the thickness T2 of the diamond single crystal board 101 shall be 100 micrometers or less. Although various etching as an etching method can be considered, 101 f of main table sides of the diamond single crystal board 101 are especially etched by reactive ion etching preferably. 101 f of main table sides by which reactive ion etching is carried out are {100} sides. The gas used for reactive ion etching is including [either / at least / carbon fluoride or argon and oxygen] mixed gas, and, as for the rate of oxygen in mixed gas, it is preferred that it is 50% or less in a volume ratio. As for this reactive ion etching, it is preferred that internal pressure is performed within a container of 6.7 Pa or less.
[0056]With reference to drawing 3, the diamond single crystal 102 is formed with a vapor phase synthetic method on the main table side 101f of the diamond single crystal board 101.
[0057]In the manufacturing method of the diamond single crystal according to this embodiment of the invention 1 constituted in this way. In order that the thickness T2 may manufacture the diamond single crystal 102 on the main table side 101f of the diamond single crystal board 101 of 100 micrometers or less, modification and a crack stop arising in the diamond single crystal 102. Therefore, even if area becomes large, a quality diamond single crystal can be provided.
[0058](Embodiment 2) Drawing 4 and drawing 5 are the sectional views for explaining the manufacturing method of the diamond single crystal according to this embodiment of the invention 2. With reference to drawing 4, the diamond single crystal object 111 is prepared first. On this diamond single crystal object 111, the thickness T2 forms the diamond single crystal board 101 of 100 micrometers or less with a vapor phase synthetic method.
[0059]The diamond single crystal object 111 is removed with reference to drawing 5. Although various etching can be considered as the method of this removal, the diamond single crystal object 111 is especially removed by reactive ion etching preferably. The gas used for reactive ion etching is mixed gas containing either [at least] carbon fluoride or argon and oxygen, and the percentage of oxygen in mixed gas is 50% or less in a volume ratio. This reactive ion etching is preferred and internal pressure is performed within a container of 6.7 Pa or less. Thickness is 100 micrometers or less including the hydrogen atom whose rate of as opposed to a carbon atom and a carbon atom in the diamond single crystal board 101 is not less than 10 ppm 500 ppm or less in an atomic ratio. 101 f of main table sides of the diamond single crystal board 101 are {100} sides. The length of at least one neighborhood of the diamond single crystal board 101 is not less than 10 mm. The diamond full width at half maximum

by the X-ray diffraction method of the diamond single crystal board 101 is 400 or less seconds 5 seconds or more.
[0060]Then, the diamond single crystal 102 as shown by drawing 3 on this diamond single crystal board 101 is grown up.
[0061]In the manufacturing method of the diamond single crystal according to this embodiment of the invention 2 provided with such a process, there is the same effect as the manufacturing method of the diamond single crystal according to Embodiment 1.
[0062]
[Example](Example 1) This example explains the process of manufacturing a 100-micrometer-thick diamond single crystal board from a high-temperature-high-pressure synthetic diamond monocrystal substrate. First, both lengths of two sides of the direction to which 500 micrometers, thickness, and thickness cross at right angles prepared as a substrate the high-temperature-high-pressure composition Ib type diamond single crystal board (sample 1) of rectangular parallelepiped shape which is 11 mm. The 6th page of a plane direction is {100}. In the surface, mechanical polish was made and surface surface roughness Rmax was 0.1 micrometer or less. Drawing 6 is a mimetic diagram of the reactive ion etching system used in Example 1. With reference to drawing 6, the reactive ion etching system 1, The vacuum chamber 10 as a container, and RF generator 11 which supplies electric power to the vacuum chamber 10, The electrode 12 arranged so that it may be connected to RF generator 11 and may face mutually within the vacuum chamber 10, It has the gas supply line 14 for supplying material gas in the vacuum chamber 10, the gas exhaust pipes 15 which discharge gas from the vacuum chamber 10, and the pressure control valve 16 which is connected to the gas exhaust pipes 15 and controls the pressure in the vacuum chamber 10.
[0063]The reactive ion etching system 1 shown by drawing 6 is a device discharge type [between RF electrodes]. Regardless of the flow of introductory gas, the pressure in a chamber is controllable by the pressure control valve 16. The diamond single crystal board 101 of the sample 1 is laid on the electrode 12. Reactive ion etching of the diamond single crystal board 101 was performed by introducing O_2 gas and CF_4 gas from the gas supply line 14 using this reactive ion etching system 1. An etching condition is as being shown in the following conditions 1.
[0064](Conditions 1)
High frequency frequency :. 13.56-MHz high-frequency power :. 300W vacuum chamber internal pressure: -- 3.3PaO_2 gas mass flow: -- 10sccm(standard cubic centimeter per minutes) CF_4 gas mass flow:, when it etches on condition of 30sccm **** for 100 hours, The high frequency discharge 17 occurred and the thickness of the diamond single crystal board 101 was set to 100 micrometers. Surface roughness Rmax of the etching surface was 0.2 micrometer.
[0065]The diamond single crystal board of 10-micrometer-thick sheet metal was able to be formed by carrying out additional

etching of the substrate of the sample 1 after this etching on the conditions. The diamond single crystal board of this sheet metal can be handled with tweezers etc. Thickness was able to make it grow epitaxially without abnormal growth to 100 micrometers, as a result of growing homoepitaxially with a microwave plasma CVD method to an etching surface.
[0066]Here, the sample 1, construction material, a size, etc. prepared the completely same sample 2 as a comparative example. Thickness of this sample 2 was made thin by mechanical polish. After polish of 400 hours, although thickness was set to 100 micrometers, the sample 2 after processing broke and decomposed it for the load at the time of polish.
[0067]As mentioned above, it was shown by by processing the diamond single crystal board of a large area by an etching process comparatively that thickness can produce a single crystal thin film board of 100 micrometers or less.
[0068](Example 2) This example explains the example which changed the etching condition in Example 1. All the diamond single crystal boards that, as for the common etching condition in this example, 13.56 MHz and high-frequency power used by 300W in high frequency frequency are the same as that of the sample 1 which is a high voltage synthetic diamond monocrystal substrate. About two or more samples, the composition ratio of etchant was changed variously, and by adjusting etching time, it etched until thickness was set to 100 micrometers. The result of having performed 100-micrometer-thick epitaxial growth at a microwave plasma CVD method to the etching surface after the granularity of an etching condition and the surface after etching and etching is shown in Table 1. The result (result of the sample 1) of Example 1 is added to Table 1 as a standard result.
[0069]
[Table 1]

ｻﾝﾌﾟﾙ No.	ｴｯﾁﾝｸﾞ条件					ｴｯﾁﾝｸﾞ結果	ｴﾋﾟ成長結果
	O_2流量 (sccm)	CF_4流量 (sccm)	Ar 流量 (sccm)	圧力 (Pa)	ｴｯﾁﾝｸﾞ時間 (時間)	面荒さ Rmax (μm)	
1	10	30	0	3.3	100	0.2	◎
3	10	10	0	3.3	50	0.3	◎
4	10	8	0	3.3	48	0.35	○
5	10	0	0	3.3	30	計測不可 (針状突起)	×
6	10	0	10	3.3	100	0.3	◎
7	10	0	8	3.3	95	0.35	○
8	10	30	0	6.7	50	0.3	◎
9	10	30	0	7.0	48	0.35	○
10	10	30	0	1.3	200	0.10	◎

ｴﾋﾟ成長結果の記号：◎全面ｴﾋﾟ成長、○一部異常成長、
×全面異常成長(多結晶)

[0070]The flows of CF_4 in an etching condition differ in the sample 1 in Table 1, and 3-5. If the ratio of CF_4 to O_2 increases, it

is shown that the surface after etching becomes flat. If the mixture ratio of O_2 gas is 50% or less of samples 1 and 3 in a volume ratio, it can grow epitaxially to an etching surface after etching. Since it will be ruined if the rate of O_2 gas ratio exceeds 50% by a volume ratio, epitaxial growth becomes difficult in this field. The samples 6 and 7 at the time of adding Ar instead of CF_4 of this tendency are also equivalent. Since a needlelike projection is formed in an etching surface when it etches only by O_2 especially, subsequent epitaxial growth becomes impossible.

[0071]If the result of the sample 1 and the samples 8-10 is compared, it understands how a pressure influences etching. That is, when the surface after etching was ruined and it became higher than especially 6.7 Pa so that chamber internal pressure was high, it turned out that subsequent epitaxial growth becomes difficult. If a pressure is lowered to 1.3 Pa, it is maintainable even after etching surface roughness almost equivalent to etching before. However, a considerable quantity of etch rates fall. However, from mechanical polishing work, it is a high speed even in this case.

[0072](Example 3) The process of thickness growing up the epitaxial film as a diamond single crystal board of 100 micrometers or less into a diamond single crystal object, and carrying out etching removal of the diamond single crystal object in this example, The characterization of the diamond single crystal board obtained in this process is explained.

[0073]First, the same diamond single crystal board as the sample 1 used in Example 1 was prepared. This diamond single crystal board was manufactured by high-temperature-high-pressure composition, and each field was {100} sides. Vertical x horizontal x thickness of the size was 11mmx11mmx0.5mm.

[0074]Drawing 7 is a mimetic diagram of the microwave plasma CVD system used in Example 3. With reference to drawing 7, the microwave plasma device 2, The vacuum chamber 20 and the microwave power supply 21 for supplying microwave to the vacuum chamber 20, The waveguide 22 which connects the microwave power supply 21 and the vacuum chamber 20, The microwave introducing window 23 for introducing microwave into the vacuum chamber 20 from the waveguide 22, It has the substrate supporting stand 25 for supporting a substrate, the gas supply line 27 which supplies material gas in the vacuum chamber 20, the gas exhausting pipe 28 which discharges gas from the vacuum chamber 20, and the pressure gauge 29 which measures the pressure in the vacuum chamber 20.

[0075]The diamond single crystal object 111 was laid on the substrate supporting stand 25, H_2 gas and CH_4 gas were supplied from the gas supply line 27, and the diamond was grown epitaxially with the microwave plasma CVD system shown by drawing 7. A growing condition is as being shown on condition of [2] the following.

[0076](Conditions 2)

microwave frequency: -- 2.45-GHz microwave power supply: -- 5-kW chamber internal pressure: -- $1.33x10^{4}PaH_2$ gas mass flow: -- $100sccmCH_4$ gas mass flow:, when it is made to grow up by the growing condition of 5sccm above for 20 hours, The microwave plasma 24 occurred and the thickness of the epitaxial film which constitutes a diamond single crystal board was set to 100 micrometers. At this time, there is no abnormal growth in a grown surface, and complete epitaxial growth was performed.
[0077]As the comparative example 2, the diamond single crystal object and the growing condition were the same, and when they made growth time 22 hours, and the thickness of the epitaxial film was 110 micrometers, the diamond single crystal object and the epitaxial film broke and decomposed them. Thus, if thickness is 100 micrometers or less, epitaxial growth of a diamond is possible on a high voltage composition single crystal body.
[0078]About the diamond single crystal board in which this thickness is 100 micrometers, etching removal of the high voltage composition single crystal portion (diamond single crystal object) was carried out by the same method as reactive ion etching applied to the sample 1 in Example 1. As a result, the diamond single crystal board with which thickness was formed by epitaxial growth at 100 micrometers was obtained.
[0079]The sample which performed mechanical polishing work instead of etching removal as the comparative example 3, and removed the diamond single crystal object was obtained. In this sample, when the thickness of the portion of an epitaxial film was set to 100 micrometers or less, it decomposed during polish, without the ability to maintain integrity as an epitaxial substrate.
[0080]As mentioned above, producing the diamond single crystal board of only an epitaxial film was shown by by also processing the epitaxial film formed in the diamond single crystal object with a comparatively large area by an etching process.
[0081]The absorptivity of the infrared light field was searched for with the infrared penetration spectrum about the epitaxially grown diamond single crystal board obtained by the above-mentioned method. The result is shown in drawing 8.
[0082]By the present, by combination with the carbon atom in a diamond, and the hydrogen atom incorporated during the crystal. Absorption peculiar to an infrared region appears and the method of quantifying the amount of hydrogen atoms under crystal from the absorption index is clarified, for example by J.KGray and SPIE (Vol.1759 Diamond Optics V (1992), P.203). It was checked that a result and 100 ppm of hydrogen atoms are contained to a carbon atom by this method in fixed quantity in the hydrogen quantity in an epitaxial film in the bottom. It checked that the half breadth of the diffraction peak (what is called a rocking curve) of the field (400) of the diamond by 2 crystal X-ray diffraction method was 30 seconds.
[0083]Drawing 9 is a graph which expands and shows the portion enclosed with IX in drawing 8. It is clear that the absorption 30 by CH_2 combination in drawing 9 has appeared.

[0084]various in the gas mass flow and growth time of CH_4 -- what -- the hydrogen concentration of the epitaxial film which made change and was formed, the half breadth of a rocking curve, and the state of the grown surface were measured. Other growing conditions are the same as the growing condition 2, and all epitaxial thickness could be 100 micrometers. The result is shown in Table 2.
[0085]
[Table 2]

ｻﾝﾌﾟﾙ No.	CH_4 流量 (sccm)	成長時間 (時間)	水素濃度 (ppm)	ﾛｯｷﾝｸﾞｶｰﾌﾞ 半値幅(秒)	成長面状態
11	5	20	100	30	◎
12	1	100	10	500	○
13	2	50	30	300	◎
14	10	10	200	200	◎
15	20	5	>1000	(多結晶)	×

成長面状態：◎異常成長なし、○一部異常成長、×多結晶

[0086]As shown in Table 2, the hydrogen concentration of good epitaxial self-supported film was settled in the not less than 30 ppm range of 200 ppm or less, and the half breadth of the X-ray rocking curve was 300 or less seconds 30 seconds or more. Especially epitaxial self-supported film (film to which "O" was attached in the column of a crystal growth side) excellent in the crystal growth state was transparent to the ultraviolet region with a wavelength of 225 nm, and was the characteristic applicable also to an optical application.
[0087](Example 4) This example explains the example to which vapor phase synthesis of the diamond single crystal was carried out from the 100-micrometer-thick tabular seed crystal.
[0088]As the sample 16, the silicon single crystal substrate as a tabular seed crystal with a diameter of 3 inches (7.62 cm) and a thickness of 100 micrometers was prepared. The plane directions of a substrate are {100} sides. The orientation nucleation was performed to the sample 16 with the hot filament CVD method which can impress board bias first. As a result, diamond membrane thickness obtained the hetero epitaxial board for your kind consideration with which the diamond plane direction was equal to {100} at 10 micrometers. Next, heteroepitaxial growth was continued using the microwave plasma CVD system (refer to drawing 7) used in Example 3. The growing condition is the same as that of the above-mentioned (conditions 2). Diamond membrane thickness was set to 100 micrometers by making growth time into 18 hours. The orienting film was united and turned into an epitaxial film of one. Then, when FUTSU nitric acid was impregnated and the silicon substrate was removed, epitaxially grown diamond self-supported film was obtained.
[0089]As the comparative example 4, thickness performed terrorism epitaxial growth from the same silicon single crystal wafer as the sample 16 to the same diamond as the above-mentioned process at 150 micrometers except it. As a result, when diamond membrane thickness exceeded 100 micrometers,

diamond membrane was disassembled with the silicon substrate. As mentioned above, it was shown that the process to which thickness carries out vapor phase epitaxy of the diamond single crystal from a tabular seed crystal of 100 micrometers or less is effective.

[0090](Example 5) By this example, thickness explains the example to which vapor phase epitaxy of the diamond single crystal was carried out from a diamond single crystal board of 100 micrometers or less.

[0091]The diamond single crystal board used for vapor phase epitaxy is two, the sample 17 and the sample 18. A length of two sides which produced the sample 17 in Example 1 and with which thickness is 10 micrometers and intersects perpendicularly is 11 mm, and the plane direction of a main table side is a high-temperature-high-pressure synthetic diamond monocrystal substrate of {100}. The length whose thickness which produced the sample 18 in Example 3 is 100 micrometers and two sides is [the plane direction of 11 mm and a main table side] an epitaxial diamond single crystal board of {100}. The half breadth of the X-ray rocking curve of the samples 17 and 18 was 10 seconds and 30 seconds, respectively. The hydrogen atom concentration under crystal of the sample 18 was 100 ppm.

[0092]The sample 18 carried out [field side where the epitaxial growth face ground the sample 17 mechanically] the epitaxial growth face side from the first. It grew homoepitaxially by the same method as Example 4 to the sample of these diamond single crystal boards. The growing condition is the same as that of the conditions 2. Making membrane formation time into 20 hours, the thickness of each epitaxial growth layer does not have abnormal growth all over being set to 100 micrometers, and did not change a substrate, either.

[0093]Here, a length of two sides a length and the thickness of a substrate cross at right angles at 500 micrometers performed the homoepitaxial growth as an above-mentioned process with plane direction of a main table side same on the high-temperature-high-pressure synthetic diamond single crystal of {100} sides at 11 mm as the comparative example 5. As a result, when epitaxial thickness was 110 micrometers, the substrate and the epitaxial film broke and decomposed during growth. From the above result, it was shown that the process to which thickness carries out vapor phase epitaxy of the diamond single crystal from a diamond single crystal board of 100 micrometers or less is effective.

[0094]It should be thought that the embodiment and example which were indicated this time are [no] illustration at points, and restrictive. The range of this invention is shown by the above-mentioned not explanation but claim, and it is meant that a claim, an equivalent meaning, and all the change in within the limits are included.

[0095]

[Effect of the Invention]As explained above, if the manufacturing method and diamond single crystal board of a diamond single crystal about this invention are used, a diamond single crystal

with it can be manufactured without a crack, modification, etc. arising in crystal growth. [a large area and] [quality]

[Translation done.]